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Molecular Oxygen as Mediator in the Metal Nanoparticles' Electrosynthesis in *N*,*N*-Dimethylformamide

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Abstract—Ultra-fine gold (<2 nm), silver (5 ± 2 nm), and palladium (<1–2 nm) nanoparticles stabilized in polyvinylpyrrolidone shell were synthesized in *N*,*N*-dimethylformamide, using molecular oxygen dissolved in the electrolyte as mediator, by the reduction of the metals' ions and complexes at the controlled potential of the oxygen reduction to its radical-anion. Pd-nanoparticles showed high catalytic activity in the reactions of *p*-nitrophenol reduction and Suzuki cross-coupling. Long-term ageing of spherical Ag-nanoparticles for 60 days in the post- electrolysis solution resulted in their consolidation (up to 17 ± 5 nm; the average size of crystallites 7.5 (3) nm). Upon similar exposure of Au-nanoparticles for 15 days, V-shaped nanoparticles were formed (length 112 ± 53 nm, width 58 ± 22 nm, crystallites 20(2)–31(1) nm); upon the isolation, dispersing into ethanol, and exposure for 48 h, hexagonal nanoparticles (105 ± 29 nm) and polygons (56 ± 25 nm, crystallites 24(2) – 51(1) nm; upon dispersing into water and exposure for 8 h, spherical nanoparticles (13 ± 8 nm, crystallites 7(1)–13.4(5) nm). Thus obtained nanoparticles are characterized by methods of cyclic voltammetry, dynamic light scattering, scanning and high resolution transmission electron microscopy, and X-ray powder diffraction.

Keywords: electrosynthesis, nanoparticles, gold, silver, palladium, mediator, oxygen, polyvinylpyrrolidone

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INTRODUCTION

Chemical reduction of metal ions and complexes is the most needed method for synthesis of the metal nanoparticles in the solution bulk [1–7]. Electrochemical reduction of the metal ions and complexes to the metal(0) is thoroughly studied, easily realizable and scalable, and is widely used in the obtaining of metals, metal blacks, electrodeposits, metal refining [8], metal nanoparticles at electrode surfaces [9]; rather rarely, for the metal nanoparticles' electrosynthesis in solution bulk, however. The main problem restricting the usage of electrochemistry to these purposes is the generated metal deposition onto the electrode surface. Some approaches to the solving of the problem are suggested. In the pulse sonoelectrochemistry method [10–12], a combination of the nanoparticles recovery at the electrode surface during short-time electroreduction, with their subsequent transfer to solution by means of the electrode sonication, is used. In the Reetz method [13–17], the ion electroreduction is carried out in aprotic organic media with the using of surface-active cations (tetraalkylammonium or -phosphonium) salts as a supporting electrolyte. In the mediated electrosynthesis method [18–31], the metal ion reduction stage is moved from the electrode surface to the solution bulk. In the latter case it is the mediator that was reduced at cathode; the mediator's reduced form diffused to the solution bulk where it reduced the metal ions or complexes. Thus, the metal deposition at a cathode is minimized or fully excluded. The method effectiveness was demonstrated by example of production of nanoparticles of Pd [18–23], Ag [24–27], Co [28], Au [29, 30], and Pt [31]. The mediators were: methyl viologen, tetraviologen calyx [4]resorcine, viologen-containing polymer nanoparticle, antracene, and fullerene C_{60}.

Recently the basic possibility of the using of molecular oxygen as a mediator in the metal nanoparticles' electrosynthesis by the reduction of the metal ions and complexes in aprotic media was demonstrated by example of Au-nanoparticles' electrosynthesis in *N*,*N*-dimethylformamide (DMF) [32]. The reduction was carried out at the controlled potential of